

PATENT SPECIFICATION

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 (72) Inventors JOHN HOWARTH MOORE and MALCOLM ROCHE

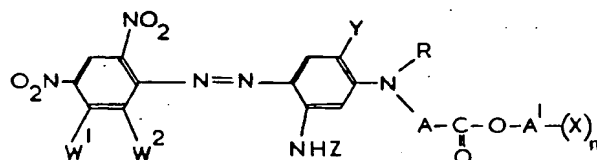


(54) DISPERSE MONOAZO DYESTUFFS

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, Imperial Chemical House, Millbank, London SW1P 3JF, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to water-insoluble monoazo dyestuffs which are valuable for colouring synthetic textile materials, in particular aromatic polyester textile materials.

According to the invention there are provided the water-insoluble monoazo dyestuffs, free from sulphonic and carboxylic acid groups, which are of the formula:—



wherein W¹ is hydrogen, chlorine, bromine, cyano or an acylamino group of the formula NHZ¹, and W² is hydrogen, chlorine, bromine, cyano or nitro, provided that either W¹ or W² is hydrogen; Z and Z¹ each independently represent acyl groups of the formula —COV or —SO₂U; V is a hydrogen atom of an amino group or a lower alkyl, lower alkoxy, phenyl or phenoxy radical which can contain substituents; U is a lower alkyl or phenyl radical which can contain substituents; Y is hydrogen, lower alkyl or lower alkoxy;

R is an alkenyl radical containing from 3 to 10 carbon atoms;

A is an alkylene radical containing from 1 to 6 carbon atoms;

n is 1 or 2, and A¹ represents a di- or tri-valent alkane radical, depending on the value of n, containing up to 4 carbon atoms;

and X is cyano, lower alkoxy, optionally substituted phenoxy, hydroxy, chlorine, bromine, lower alkoxycarbonyl, optionally substituted phenoxy-carbonyl, carbonamido (carbamoyl), optionally substituted carboanilido, N-lower alkyl or N:N-di lower alkyl carbonamido, amino, optionally substituted anilino, N-lower alkylamino, N:N-di lower alkylamino, lower alkylsulphonyl, optionally substituted phenylsulphonyl or a radical of the formula U.CO—, U.COO— or UCONH—.

Throughout this Specification the terms "lower alkyl" and "lower alkoxy" are used to denote alkyl and alkoxy radicals respectively containing from 1 to 4 carbon atoms.

As examples of the lower alkyl radicals represented by U, V and Y there may be mentioned methyl, ethyl, n-propyl and n-butyl, and as examples of the lower alkoxy radicals represented by V and Y there may be mentioned n-propoxy, n-butoxy and preferably ethoxy and methoxy. As examples of the substituted lower alkyl radicals represented by U and V there may be mentioned hydroxy lower alkyl such as β-hydroxy-ethyl, lower alkoxy lower alkyl such as β-(methoxy or ethoxy) ethyl and p-methoxypropyl, cyano lower alkyl such as β-cyano-ethyl, and aryl

lower alkyl such as benzyl and β -phenylethyl. As examples of the substituted phenyl radicals represented by U and V there may be mentioned tolyl, anisyl, chlorophenyl and bromophenyl. As examples of the substituted phenoxy radicals represented by V there may be mentioned chlorophenoxy and bromophenoxy.

It is however preferred that Z and Z' each independently represent a lower alkyl carbonyl radical.

The alkenyl radicals represented by R preferably contain 3 or 4 carbon atoms, for example allyl and crotonyl radicals.

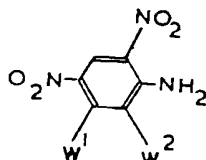
Examples of the radicals represented by X include lower alkoxy such as methoxy, ethoxy, propoxy and butoxy, lower alkoxy carbonyl such as methoxycarbonyl and ethoxycarbonyl (carboethoxy), optionally substituted phenoxy carbonyl such as phenoxycarbonyl itself and chloro- or bromophenoxy carbonyl, optionally substituted carboanilido such as carboanilido itself and carbo-anisidino and carbo-toluidino, lower alkyl carbonamido such as N-methyl-, N-ethyl-, N,N-dimethyl- and N,N-diethylcarbonamido, optionally substituted anilino such as anilino itself and anisidino, toluidino and chloro- or bromoanilino, lower alkyl-amino such as N-methyl-, N-n-propyl-, N,N-diethyl- and N-methyl-N-ethylamino, lower alkylsulphonyl such as methylsulphonyl, optionally substituted phenylsulphonyl such as phenylsulphonyl itself and *p*-tolylsulphonyl and *m*-nitrobenzenesulphonyl, radicals of the formula $\text{UCO}-$ such as acetyl, propionyl and benzoyl, $\text{UCOO}-$ such as acetoxy, benzoyloxy and chlorobenzoyloxy, and $\text{UCONH}-$ such as acetyl amino, propionyl amino, benzoyl amino and methoxybenzoyl amino.

Preferably X is carbonamido, acetoxy, propionyloxy, butyryloxy, and, above all, cyano, lower alkoxy or lower alkoxy carbonyl.

It is however preferred that *n* represents 1, so that A' represents an alkylene radical containing from 1 to 4 carbon atoms such as methylene, propylene, trimethylene, tetramethylene, α,β -dimethylethylene, and preferably ethylene.

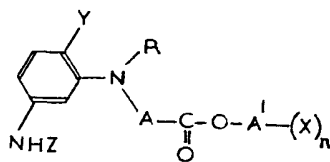
As examples of the alkylene radicals represented by A there may be mentioned methylene, trimethylene, propylene, tetramethylene, hexamethylene, α,β -dimethylethylene, and preferably ethylene. It is preferred that A and A' each represent ethylene.

According to a further feature of the invention there is provided a process for the manufacture of the water-insoluble monoazo dyestuffs of the invention which comprises diazotising an amine of the formula:—



Formula I

and coupling the resulting diazo compound with a coupling component of the formula:—



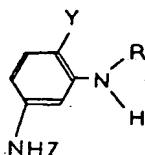
Formula II

wherein W¹, W², A, A', R, X, Y, Z and *n* have the meanings stated above.

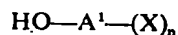
The process can be carried out by conventional methods, for example by dissolving the amine of Formula I in nitrosylsulphuric acid at a temperature in the region of 10°—25°C, and adding the resulting solution of the diazo compound to a solution of the coupling component in water containing a water-soluble organic liquid such as acetone and/or an inorganic acid such as hydrochloric acid. The pH of the mixture is then raised to effect coupling by the addition of sodium acetate and the resulting dyestuff is isolated by conventional methods.

As examples of the amines of Formula I there may be mentioned 2:4-dinitro-5-(chloro or bromo)-aniline, 2:4-dinitro-5-aminobenzonitrile, 2:4-dinitro-5-aminoacetanilide, 2:4-dinitro-6-(chloro or bromo)-aniline and 2:4-dinitro-6-cyanoaniline.

The coupling components of Formula II can be conveniently obtained by conventional methods, for example by reacting an amine of the formula:—

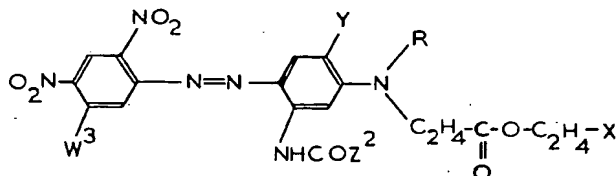


with one molecular proportion of a halogen alkanic acid or acrylic acid and esterifying the resulting acid with an alcohol of the formula:—



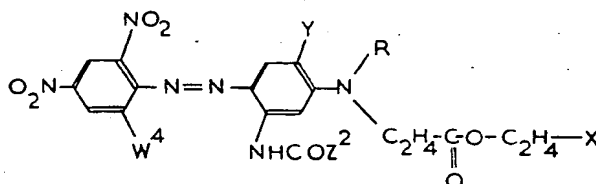
As specific examples of the said coupling components there may be mentioned 2 - (methyl, methoxy or ethoxy) - 5 - (formylamino or acetyl amino) - N - allyl - N - [β - (β' - methoxyethoxycarbonyl)ethyl]aniline, 3 - acetyl amino - N - allyl - N - [β - (β' - phenoxyethoxycarbonyl)ethyl]aniline, 3 - acetyl amino - N - (β - methylallyl) - N - [β - (cyanomethoxycarbonyl)ethyl]aniline and 2 - (methoxy or ethoxy) - 5 - (acetyl amino or propionyl amino) - N - allyl - N - (β - (β' - (acetoxy- or propionyloxy or methoxycarbonyl- or ethoxycarbonyl) - ethoxycarbonyl)ethyl]aniline.

One preferred class of the monoazo dyestuffs of the invention comprises the monoazo dyestuffs of the formula:—



wherein Y and R have the meaning stated above, Z¹ is hydrogen or lower alkyl, W³ is chlorine, bromine, cyano or —NHCOZ², and X¹ is cyano, lower alkoxy, lower alkoxy carbonyl, carbonamido, acetoxy, propionyloxy or butyryloxy.

A second preferred class of the monoazo dyestuffs of the invention comprises the monoazo dyestuffs of the formula:—



wherein Y and R have the meaning stated above, Z² is hydrogen or lower alkyl, X¹ is cyano, lower alkoxy, lower alkoxy carbonyl, carbonamido, acetoxy, propionyloxy or butyryloxy, and W⁴ is chlorine, bromine, nitro or cyano.

The monoazo dyestuffs, as hereinbefore defined, are valuable for colouring synthetic textile materials, for example cellulose acetate and cellulose triacetate textile materials, polyamide textile materials such as polyhexamethylene-adipamide textile materials, and preferably aromatic polyester textile materials such as polyethylene terephthalate textile materials. Such textile materials can be in the form of thread, yarn, or woven or knitted fabric. Preferably the dyestuffs in the form of aqueous dispersions are applied to the said materials by a dyeing, padding or printing process.

Such textile materials can conveniently be coloured with the monoazo dyestuffs, as hereinbefore defined, by immersing the textile material in a dyebath comprising an aqueous dispersion of one or more of the said dyestuffs, which dyebath preferably contains a non-ionic, cationic and/or non-ionic surface-active agent, and thereafter heating the dyebath for a period at a suitable temperature. In the case of secondary cellulose acetate textile materials it is preferred to carry out

the dyeing process at a temperature between 60° and 85°C; in the case of cellulose triacetate or polyamide textile materials it is preferred to carry out the dyeing process at 95° to 100°C; in the case of aromatic polyester textile materials the dyeing process can either be carried out at a temperature between 90° and 100°C, preferably in the presence of a carrier such as diphenyl or *o*-hydroxydiphenyl, or at a temperature above 100°C, preferably at a temperature between 120 and 140°C under superatmospheric pressure.

Alternatively the aqueous dispersion of the said monoazo dyestuff can be applied to the textile material by a padding or printing process, followed by heating or steaming of the textile material. In such processes it is preferred to incorporate a thickening agent, such as gum tragacanth, gum arabic or sodium alginate, into the aqueous dispersion of the said monoazo dyestuff.

At the conclusion of the colouring process it is preferred to give the coloured textile material a rinse in water or a brief soaping treatment before finally drying the coloured textile material. In the case of aromatic polyester textile materials it is also preferred to subject the coloured textile material to a treatment in an alkaline aqueous solution of sodium hydrosulphite before the soaping in order to remove loosely attached dyestuff from the surface of the textile material.

The monoazo dyestuffs have excellent affinity and building up properties on synthetic textile materials, and in particular on aromatic polyester and acetate rayon textile materials, so enabling deep shades to be obtained. The resulting colourations have excellent fastness to light, to wet treatments, and, in particular, to dry heat treatments such as those carried out at high temperatures during pleating operations.

If desired the dyestuffs of the invention can be applied to synthetic textile materials in conjunction with other disperse dyes, such as are described in, for example, British Specification Nos. 806271, 835819, 840903, 847175, 852396, 852493, 859899, 865328, 872204, 89012, 908656, 910306, 913856, 919424, 944513, 944722, 953887, 959816, 960235 and 961412.

The invention is illustrated but not limited by the following Examples in which all the parts are by weight:—

Example 1.

2.2 Parts of 2:4-dinitro-5-chloroaniline are added to nitrosylsulphuric acid, which is obtained by dissolving 0.7 part of sodium nitrite in 8 parts of sulphuric acid monohydrate at 15°C, and the mixture is stirred for 2 hours at 10°C to 15°C. The solution so obtained is added to a solution of 3.5 parts of 2-methoxy-5-acetyl-amino-N-allyl-N-[β -(β' -methoxyethoxycarbonyl)ethyl]aniline in a mixture of 150 parts of water and 60 parts of acetone at 5°C, sodium acetate then being added to raise the pH to 4, and the mixture is stirred for 60 minutes. The dyestuff is then filtered off, stirred in an aqueous solution of sodium carbonate, and the precipitated dyestuff is filtered off, washed with water and dried.

When dispersed in aqueous medium the dyestuff has excellent affinity for polyethylene terephthalate textile materials which it dyes in navy blue shades having excellent fastness to dry heat treatments, and to light.

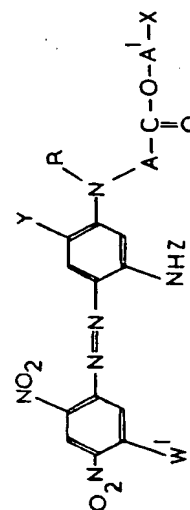
The 2-methoxy-5-acetyl-amino-N-allyl-N-[β -(β' -methoxyethoxycarbonyl)ethyl]aniline used in the above Example was obtained by reacting 2-methoxy-5-nitro-N-allylaniline with acrylic acid, esterifying the resulting product with β -methoxyethanol in sulphuric acid, reducing the nitro group to an amino group and finally acylating using one molecular proportion of acetic anhydride in pyridine at 20°C.

Table I gives further Examples of the dyestuffs of the invention which are obtained by diazotising the amines listed in the second column of the Table and coupling the resulting diazo compounds with the coupling components listed in the third column of the Table using methods similar to that described in Example 1. The fourth column of the Table gives the shades obtained when the dyestuffs are applied to polyester textile materials.

TABLE I

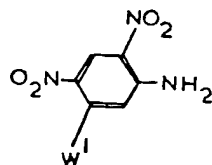
Example	Amine	Coupling Component	Shade
2	2:4-dinitro-6-bromoaniline	2-methoxy-5-acetylamino-N-allyl-N- β -(β' -methoxyethoxycarbonyl)ethyl)aniline	Greenish-blue
3	"	2-methoxy-5-acetylamino-N-allyl-N- β -(β' -ethoxyethoxycarbonyl)ethyl)aniline	"
4	"	2-methoxy-5-acetylamino-N-(β -methylallyl)-N- β -(β' -methoxyethoxycarbonyl)ethyl)aniline	"
5	"	2-methoxy-5-acetylamino-N-allyl-N- β -(β' -hydroxyethoxycarbonyl)ethyl)aniline	"
6	2:4:6-trinitroaniline	2-methoxy-5-acetylamino-N-allyl-N- β -(β' -methoxyethoxycarbonyl)ethyl)aniline	"
7	2:4-dinitro-6-cyanoaniline	"	"
8	"	3-propionylamino-N-allyl-N- β -(β' -methoxyethoxycarbonyl)ethyl)aniline	"
9	2:4-dinitro-6-chloroaniline	2-ethoxy-5-acetylamino-N-allyl-N- β -(β' -methoxyethoxycarbonyl)ethyl)aniline	"
10	2:4-dinitro-6-cyanoaniline	"	"
11	2:4:6-trinitroaniline	2-methoxy-5-acetylamino-N-allyl-N- β -(dicyanomethoxycarbonyl)ethyl)aniline	Navy Blue

Table II gives further Examples of the dyestuffs of the invention of the formula:—



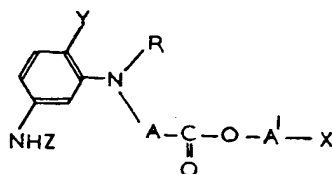
the symbols of which have the values given in the respective columns of the Table, and the last column of which gives the shades obtained when the dyestuffs are applied to an aromatic polyester textile material. The dyestuffs of these Examples were obtained by diazotising the appropriate amine of the formula:—

5



5

and coupling the resulting diazo compound with the appropriate coupling component of the formula:—



using methods similar to that described in Example 1.

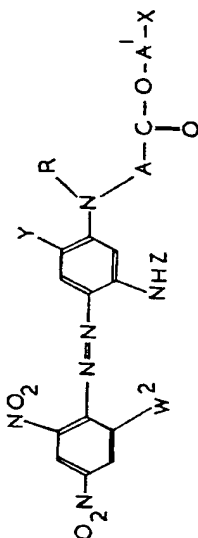
TABLE II

Example	W ¹	Z	Y	A	A ¹	X	R	Shade
12	bromine	acetyl	methoxy	ethylene	ethylene	methoxy	allyl	Navy-blue
13	acetyl amino	"	"	"	"	"	"	"
14	cyano	"	"	"	"	ethoxy	"	"
15	β -chloropropionyl amino	propionyl	ethoxy	"	"	methoxy	"	"
16	methylsulphonyl-amino	acetyl	methoxy	"	"	"	"	Reddish-blue
17	benzoyl amino	"	"	"	"	hydroxy	"	"
18	chlorine	"	"	"	"	methoxy	β -methyl-allyl	Navy-blue
19	"	"	"	trimethylene	"	"	allyl	"
20	"	"	"	ethylene	tetramethylene	acetyloxy	"	"
21	"	"	ethoxy	"	ethylene	cyano	"	"
22	"	"	methoxy	β -methyl ethylene	"	propionyl-oxy	"	"
23	"	"	"	ethylene	"	phenoxy	"	"
24	"	ethoxycarbonyl	"	"	"	methoxy	"	"
25	"	β -chloropropionyl	"	"	"	"	β -methyl-allyl	"
26	"	benzoyl	"	"	"	"	allyl	"
27	"	p-toluenesulphonyl	"	"	"	"	"	"

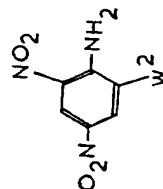
TABLE II (Continued)

Example	W ¹	Z	Y	A	A ¹	X	R	Shade
28	Chlorine	carbonamido	methoxy	ethylene	ethylene	methoxy	allyl	Navy-blue
29	"	acetyl	methyl	"	"	"	"	Violet
30	"	"	ethyl	"	"	"	"	"
31	"	"	hydrogen	"	"	"	"	"

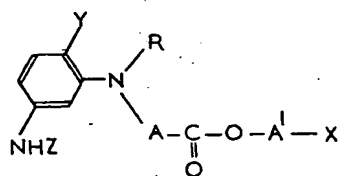
Table III gives further Examples of the dyestuffs of the invention of the formula:



5 the symbols of which have the values given in the respective columns of the Table, and the last column of which gives the shades obtained when the dyestuffs are applied to an aromatic polyester textile material. The dyestuffs of these Examples were obtained by diazotising the appropriate amine of the formula:—



and coupling the resulting diazo compound with the appropriate coupling component of the formula:—



using methods similar to that described in Example 1.

TABLE III

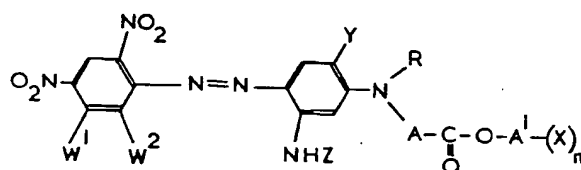
Example	W ²	Z	Y	A	A'	X	R	Shade
32	chlorine	acetyl	methoxy	ethylene	ethylene	methoxy	allyl	Navy-blue
33	bromine	propionyl	ethoxy	"	"	"	"	"
34	"	β -chloropropionyl	methoxy	"	"	"	"	"
35	"	ethoxycarbonyl	"	"	"	"	"	"
36	"	benzoyl	"	"	"	"	"	"
37	"	<i>p</i> -toluenesulphonyl	"	"	"	"	"	"
38	"	carbonamido	"	"	"	"	"	"
39	"	acetyl	methyl	"	"	"	"	"
40	"	"	hydrogen	"	"	"	"	Reddish-blue
41	"	"	methoxy	trimethylene	tetramethylene	acetoxo	"	Violet
42	"	"	"	β -methylethylene	trimethylene	methoxy	"	Navy-blue
43	"	"	"	ethylene	ethylene	hydroxy	β -methyl-allyl	"
44	"	"	"	"	"	acetyloxy	allyl	"
45	"	"	"	"	"	propionyloxy	"	"
46	"	"	"	"	"	ethoxy	"	"
47	"	"	"	"	"	phenoxy	"	"
48	"	"	"	"	"	cyano	"	"
49	"	"	"	"	trimethylene	"	"	"

TABLE III (Continued)

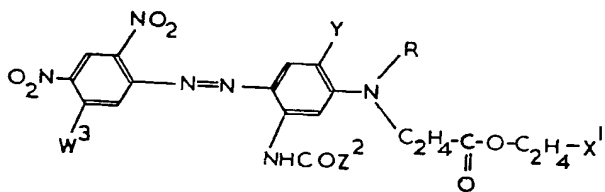
Example	W ²	Z	Y	A	A ¹	X	R	Shade
49	bromine	acetyl	methoxy	ethylene	trimethylene	cyano	allyl	Navy-blue
50	"	"	"	"	tetramethylene	"	"	"
51	"	"	"	"	ethylene	benzoyl	"	"
52	"	"	"	"	"	methoxycarbonyl carbonyl	"	"
53	"	"	"	"	"	ethoxycarbonyl	"	"
54	"	"	"	"	"	butoxycarbonyl	"	"
55	"	"	"	"	"	<i>p</i> -nitrophenoxy	"	"
56	"	"	"	"	"	chlorine	"	"
57	"	"	"	"	"	bromine	"	"
58	"	"	"	"	"	<i>m</i> -chloro- phenoxy	"	"
59	"	"	"	"	"	<i>N</i> -ethylcarba- moyl	"	"
60	"	"	"	"	"	<i>N</i> -phenylcarba- moyl	"	"
61	"	"	"	"	"	carbamoyl	"	"
62	"	"	"	"	"	anilino	"	"
63	"	"	"	"	"	ethylsulphonyl	"	"
64	"	"	"	"	"	<i>p</i> -toluenesul- phenyl	"	"
65	"	"	"	"	"	benzoylamino	"	"

WHAT WE CLAIM IS:—

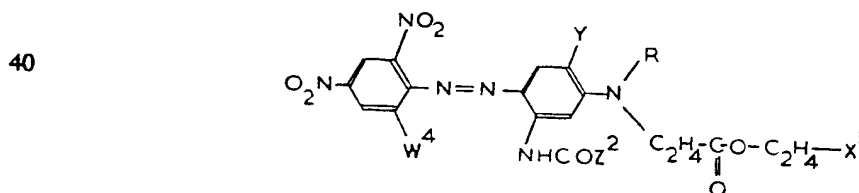
1. The water-insoluble monoazo dyestuffs, free from sulphonic and carboxylic acid groups, which are of the formula:—



- 5 wherein W¹ is hydrogen, chlorine, bromine, cyano or an acylamino group of the
formula NHZ¹, and W² is hydrogen, chlorine, bromine, cyano or nitro, provided
that either W¹ or W² is hydrogen; Z and Z¹ each independently represent acyl
10 groups of the formula —COV or —SO₂U; V is a hydrogen atom or an amino group
or a lower alkyl, lower alkoxy, phenyl or phenoxy radical which can contain
substituents; U is a lower alkyl or phenyl radical which can contain substituents; Y
is hydrogen, lower alkyl or lower alkoxy;
15 R is an alkenyl radical containing from 3 to 10 carbon atoms;
A is an alkylene radical containing from 1 to 6 carbon atoms;
n is 1 or 2, and A¹ represents a di- or tri-valent alkane radical, depending on
the value of n, containing up to 4 carbon atoms;
15 and X is cyano, lower alkoxy, optionally substituted phenoxy, hydroxy,
chlorine, bromine, lower alkoxy, optionally substituted phenoxy,
carbonyl, carbonamido (carbamoyl), optionally substituted phenoxy,
20 lower alkyl or N:N-di lower alkyl carbonamido, amino, optionally substituted
anilino, N-lower alkylamino, N:N-di lower alkylamino, lower alkylsulphonyl,
optionally substituted phenylsulphonyl or a radical of the formula U.CO—,
U.CO— or UCONH—.
2. Dyestuffs as claimed in Claim 1 wherein Z and Z¹ each independently
25 represent a lower alkylcarbonyl radical.
3. Dyestuffs as claimed in Claim 1 or Claim 2 wherein the alkenyl radical
represented by R contains 3 or 4 carbon atoms.
4. Dyestuffs as claimed in any one of Claims 1 to 3 wherein n is 1 and A¹
represents an alkylene radical containing from 1 to 4 carbon atoms.
5. Dyestuffs as claimed in any one of Claims 1 to 4 wherein A and A¹ each
30 represent an ethylene radical.
6. Dyestuffs as claimed in any one of Claims 1 to 5 wherein X is carbonamido,
acetoxy, propionyloxy, butyryloxy, cyano, lower alkoxy, or lower alkoxy carbonyl.
7. Dyestuffs as claimed in any one of Claims 1 to 6 which are of the formula:—



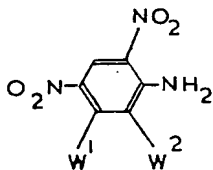
- 35 wherein Y and R have the meanings stated in Claim 1, Z² is hydrogen or lower
alkyl, W³ is chlorine, bromine, cyano or —NHCOZ², and X¹ is cyano, lower
alkoxy, lower alkoxy carbonyl, carbonamido, acetoxy, propionyloxy or
butyryloxy.
8. Dyestuffs as claimed in any one of Claims 1 to 6 which are of the formula



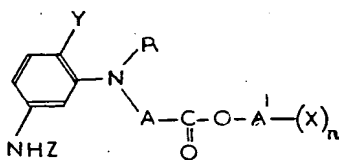
wherein Y and R have the meanings stated in Claim 1, Z² is hydrogen or lower alkyl, X¹ is cyano, lower alkoxy, lower alkoxy carbonyl, carbonamido, acetoxy, propionyloxy or butyryloxy, and W⁴ is chlorine, bromine, nitro or cyano.

9. Dyestuffs as claimed in any one of Claims 1 to 8 substantially as described herein and shown with reference to any one of the Examples.

10. Process for the manufacture of the dyestuffs as claimed in Claim 1 which comprises diazotising an amine of the formula:—



and coupling the resulting diazo compound with a coupling component of the formula:—



wherein W¹, W², A, A¹, R, X, Y, Z and n have the meanings stated above in Claim 1.

11. Process for the manufacture of the dyestuffs as claimed in any one of Claims 1 to 9 substantially as described herein and shown with reference to any one of the Examples.

12. Process for colouring synthetic textile materials which comprises applying to the said textile materials by a dyeing, padding or printing process an aqueous dispersion of a dyestuff as claimed in any one of Claims 1 to 9.

13. Process as claimed in Claim 12 wherein the textile material is an aromatic polyester textile material.

D. VINCENT,
Agent for the Applicants.

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